Form Approved REPORT DOCUMENTATION PAGE OMB No. 0704-0188 Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service. Directorate for Information Operations and Reports, 1215_lefferson Davis Highway, Suite 1204, Arington, VA 22202-4302, and to the Office of Management and Budget. Paperwork Reduction Project (0704-0188) Washington, DC 20503. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS. 1. REPORT DATE (DD-MM-YYYY) 2. REPORT DATE 3. DATES COVERED (From - To) Final Report 05/22/2000 04/01/96 to 03/31/2000 4. TITLE AND SUBTITLE 5a. CONTRACT NUMBER Sub-Micron Lithography with the Atomic 5b. GRANT NUMBER Force Microscope N00014-94-1-0771 5c. PROGRAM ELEMENT NUMBER 6. AUTHOR(S) **5d. PROJECT NUMBER** N00014-94-1-0771 5e. TASK NUMBER Calvin F. Quate 5f. WORK UNIT NUMBER 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER Stanford University Sponsored Projects Office 651 Serra Street, Room 110 Stanford, CA 94305-6215 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSOR/MONITOR'S ACRONYM(S) Office of Naval Research ONR Ballston Centre Tower One 11. SPONSORING/MONITORING 800 North Quincy Street AGENCY REPORT NUMBER Arlington, VA 22217-5660 12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution unlimited. 13. SUPPLEMENTARY NOTES The views, opionions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Navy position, policy, or decision, unless so designated by other documentation. We investigated methods for fabricating nanoscale devices with feature sizes below 100nm. It was based on scanning probes as fabricated in our own facility. It was known from the beginning that the intense field at the tip of the probe could be used to selectively oxidize silicon if it was first passivated with hydrogen. It is a lithographic process since the oxidized regions serve as the etch mask when the pattern is transferred into the substrate. We investigated other methods of patterning. The major effort was the exposure of electron resist with electrons field emitted from the tip. We determined that there was no proximity effect in Scanning Probe Lithography. In later work we able to pattern very narrow lines. With electron resist we were successful in writing lines as narrow as 26 nm. With oxidization of Titanium films (and with the use of carbon nanotubes for tips) we were successful in writing lines 6 nm in width. We, also, improved the throughput by increasing the writing speed and writing with parallel arrays of probes.

Scanning Probes, Lithography, nano scale devices, proximity effect, E-beams

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:				18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PFRSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU	OF PAGES	Calvin F. Quate
1				8	19b. TELEPONE NUMBER (Include area code)
					(650) 723-0213

Standard Form 298 (Rev. 8-98) Prescribed by ANSI-Std Z39-18

Final Report

for

Office of Naval Research

Contract Number: N00014-94-1-0771

for a program of research entitled:

Sub-Micron Lithography with the Atomic Force Microscope

Reporting Period: 04/01/96 to 03/31/2000

Principal Investigator Calvin F. Qute

Leland T. Edwares Professor in the School of Engineering (Research) and Professor, by courtesy, of Applied Physics (Research)

Edward L. Ginzton Laboratory Stanford University Stanford, CA 94305-4085 Telephone: (650) 723-0213

Fax: (650) 723-4659

E-mail: quate@stanford.edu

ONR/DARPA Final Report May 2000

I. Introduction

In this program we undertook the investigation of methods for fabricating nanoscale devices with feature sizes below 100nm. The investigation was based on various forms of scanning probes as fabricated in our own facility. It was known from the beginning that the intense field at the tip of the probe could be used to selectively oxidize silicon if it was first passivated with hydrogen. It is believed that the field at the tip desorbs the hydrogen and exposed clean silicon. The E field also ionizes water molecules in the vicinity and creates negative OH ions. These serve to enhance the rate of oxidation of the exposed silicon. It is a lithographic process since the oxidized regions serve as the etch mask when the pattern is transferred into the substrate. During the course of this program it was determined, both here and in outside labs, that other materials could be selectively oxidized in this manner, including; polysilicon, aluminum and titanium.

We launched this program with the fabrication of operating devices using the scanning probe tips to lithographically define the gate region. By writing a narrow line of oxide on the gate material (polysilicon) we were able to fabricate a MOSFET with a gate length of 100 nm. It stands as the first device fabricated with the scanning probes with good electrical characteristics.

We went on from there to investigate other methods of patterning. The major effort was the exposure of electron resist, such as PMMA or SAL 601, with electrons field emitted from the tip. We uncovered several advantages for this low voltage (40 volts) system as compared to the high energy electrons used in the more conventional SEM. In a comparative study between Scanning Probe Lithography (SPL) and Electron Beam Lithography (EBL) we determined that there was no proximity effect in SPL, a powerful advantage with complex layouts.

In later work we able to pattern very narrow lines. With electron resist we were successful in writing lines as narrow as 26 nm. With oxidization of Titanium films (and with the use of carbon nanotubes for tips) we were successful in writing lines 6 nm in width.

We, also, considered the problem of throughput and approached this on two fronts. We, first, increased the writing speed by moving the tip with a higher scanning speed. And, second, we demonstrated writing with an array of probes where the tips were operated in parallel.

There are several labs working on cantilever arrays. At Stanford we have a linear array of 50 cantilevers used for imaging and for lithography. At IBM Zurich they have an array of 1024 cantilevers designed for disk storage. At DaeWoo in Korea they have piezoelectric cantilevers in an array that measures 780x1024. The DaeWoo unit is designed with a mirror on each cantilever so as to operate as a spatial light modulator for projecting optical images. There

is little doubt that micromachining techniques an be used to fabricate huge arrays of cantilevers. When these are combined with a fast scanner (5-10 mm/sec) the throughput problem that plagues this system will be resolved.

II. Improving the Throughput

Scanning probe lithography (SPL) may be used to pattern nanometer-scale features on a variety of substrates. In fact, scanning probes have been used to manipulate individual atoms, achieving perhaps the ultimate lithographic resolution. However, the serial nature of SPL makes this technology much slower than "mask" techniques such as photolithography, x-ray lithography, or extreme ultraviolet (EUV) lithography. A potential advantage of a direct write approach is that it does not require expensive and time-consuming mask fabrication. SPL may also have superior alignment capabilities. Nevertheless, in order for SPL to become a viable technique for high resolution lithography, the throughput must be dramatically increased. We believe SPL throughput can be increased by attacking the issue on two fronts: (1) by increasing the writing speed with a single tip and (2) by patterning simultaneously with multiple probes. We have previously shown that operating in the hybrid atomic force microscope (AFM) / scanning tunneling microscope (STM) lithography mode has several advantages over other SPL techniques. In this mode, both the tip-sample force and the emission current are independently controlled for resist exposure. The tip is held in contact with the resist surface to minimize beam spreading for enhanced patterning resolution. A voltage bias between the probe and the sample generates the field emission of electrons from the sharp probe tip. The voltage is varied to maintain a constant emission current. The current feedback ensures that a constant dose of electrons is delivered to the resist, yielding uniform lithography even when the resist thickness varies as a function of position. This method has since been adopted by other groups because of the improved performance and reliability. The lithographic speed is limited primarily by the bandwidth of the feedback loops used to control force and current.

Further increases in patterning throughput require simultaneous writing with multiple probes. Minne performed parallel oxidation lithography with an array of cantilevers. Since the electric-field-enhanced oxidation process is inherently slow, it may not be suitable for high throughput patterning. Finally we resolve the challenges encountered when the resist exposure scheme is extended to multiple tips with individual control of the current from each tip.

III. Control of the Tip-Sample Force

The mechanical response of the actuator that moves the probe up and down limits the

scan speed with constant force maintained. Generally, the piezotube scanner is used as the actuator. This large device typically has a resonance below 1 kHz, limiting scan speeds to less than 200 μ m/s. Manalis demonstrated that the tip velocity can be increased by at least an order of magnitude by using a piezoelectric actuator integrated onto the cantilever. Minne has used these cantilevers for high speed imaging with multiple tips where the tip-sample force was maintained simultaneously and independently by each cantilever.

As a simpler alternative, we have investigated the feasibility of performing exposure lithography in the constant-height AFM mode, where the tip is scanned in contact with the sample without controlling the tip-sample force. In Minne's work the higher forces between the tip and hard silicon sample apparently damaged the tip and degraded patterning fidelity. Because the surface of an organic resist is soft and pliable, we do not expect small variations in the applied force to damage the tip. However, excessive force between the tip and sample could cause the tip to penetrate (or scratch) the resist.

We have tested exposure lithography with and without real-time force feedback. For constant-height scanning, we lowered the tip toward the resist-coated sample until the cantilever was deflected slightly (~ 10 nN force between the tip and resist). The tip was then moved in the x-y plane of the sample and the current feedback was enabled. We have shown that lines written with and without force feedback appear to have equivalent fidelity. In fact, in some instances patterns written in the constant height mode had superior uniformity. The tip-sample bias used to generate the electron beam contributes an electrostatic force that has an adverse effect on the force feedback. We observed this effect as a variation in voltage during lithography on flat samples; the voltage is generally more steady in the constant height mode. If the cantilevers were sufficiently compliant, this constant-height scanning scheme should also work for patterning over topography. Therefore either by incorporating integrated actuators or by operating in the constant height AFM mode, the lithography speed should not be limited by the response of the force feedback. Maintaining the emission current (or exposure dose) at a fixed level during lithography at high scan speeds is a problem that must be dealt with.

IV. Tip Current Control

Our method of scanning probe lithography (SPL) uses electrons field emitted from a micromachined probe tip in air to expose organic polymer resists. Low energy electron exposure of resist by SPL has been shown to have sub-30-nm resolution, a wide exposure latitude, excellent linearity, and negligible proximity effects. The pattern dimension is set by the electron exposure dose delivered to the resist. Control of the exposing current has been achieved previously through external feedback circuitry. Typically the emission current is measured and

compared with the desired (or setpoint) current. A signal is sent to adjust either the tip-sample voltage, or the tip-sample distance in order to ensure that the measured current does not deviate significantly from the setpoint. There are a number of advantages to integrating the current source onto the cantilever chip:

Integrated current control would both simplify and miniaturize the SPL system, creating a small unit cell comprised of the electron emitter (tip) and exposure dose control (current source), eliminating the need for external circuitry. The bandwidth of the external control loop, which is hampered by parasitic capacitances, limits the lithography speed. An integrated current source could allow higher speed patterning. Integration of the SPL control on-chip would greatly facilitate the extension to parallel lithography using arrays of scanning probes. SPL throughput may be increased by patterning simultaneously with multiple probes.

We have integrated a metal-oxide-semiconductor field-effect transistor (MOSFET) onto the cantilever chip to act as a current source for control of the emission current from the tip. In the saturation regime, the MOSFET drain-to-source current is independent of the drain-to-source bias and set by the gate voltage. This property allows us to use a MOSFET as a voltage-controlled current source. We have designed and fabricated of the integrated transistor and shown that this on-chip device can be used as the sole current-control electronics for reliable SPL.

To summarize, we have demonstrated the use of this integrated transistor as the sole control electronics for stable SPL of nanometer-scale patterns in organic resist. This integrated current source eliminates the need for external feedback control circuitry and simplifies the lithography process. The integrated current source should facilitate the extension to parallel lithography with multiple scanning probes.

V. High-speed Tapping Mode

Intermittent contact mode, or tapping mode, has become the dominant mode of AFM operation because it reduces the lateral forces between the tip and sample. The cantilever drive loop controls the vertical distance between the tip and the sample. In most AFM's, the feedback loop controls a conventional piezotube such that when the sample topography causes the cantilever's RMS amplitude to change, the piezotube will extend or contract to restore the cantilever's original RMS value.

While the tapping mode AFM allows nanometer scale resolution with negligible frictional forces, it is encumbered by slow imaging speed. The scan speed of typical tapping mode AFM is limited in part by the resonant frequency of the piezotube and in part by the time it takes for the oscillating cantilever to change amplitude. (Other factors play a role in the tapping mode

imaging speed, such as the bandwidth of the RMS to dc converter, but these are secondary). For most samples, these constraints limit the tapping mode AFM's scan speed to a few tens of microns per second.

We increased the tapping mode imaging rate with two improvements. First, a faster z-axis actuator was integrated onto the cantilever and active damping circuits were applied to increase the speed at which the cantilever can respond. The speed of tapping mode with the atomic force microscope (AFM) has been increased by over an order of magnitude. The enhanced operation is achieved by (1) increasing the instrument's mechanical bandwidth and (2) actively controlling the cantilever's dynamics. The instrument's mechanical bandwidth is increased by an order of magnitude by replacing the piezotube z-axis actuator with an integrated zinc oxide (ZnO) piezoelectric cantilever. The cantilever's dynamics are optimized for high-speed operation by actively damping the quality factor (Q) of the cantilever. Active damping allows the amplitude of the oscillating cantilever to respond to topography changes more quickly. With these two advancements, high-speed tapping mode images have been obtained with a scan frequency of 15 Hz. This corresponds to a tip velocity of 2.4 mm/s.

VI. Writing with Carbon Nanotubes

We have explored an alternative method for writing lines and bits on an ultrasmooth substrate. It is well known that the tapping-mode atomic force microscope (AFM) can oxidize atomically flat titanium with a single-walled carbon nanotube to achieve high density writing. While this data rate is slow, parallelism can serve to overcome this limitation. Tapping mode is used to reduce lateral forces and permit operation with the single-walled nanotube (SWNT) tip. The nanotube tip allows for highly localized surface modification. Additionally, the extreme hardness and cylindrical shape of the nanotube alleviates degradation from tip wear during the writing process, and minimizes the effects of tip convolution.

Lines were written in titanium using the electric field from the conductive nanotube to locally oxidize the titanium surface. Field-induced oxidation was originally developed on silicon with the STM by Dagata and on titanium with the STM by Sugimura With this method a scanning probe is brought in close proximity to a thin metal film and a negative bias voltage is applied to the probe tip in the presence of water adsorbed on the surface. As reported in previous progress reports, local oxidation has been well characterized in terms of parameters such as tip diameter, substrate roughness, field strength, scanning rate, tip—sample distance, and environment. However, the diameter of the proximal probe tip and the surface roughness of the substrate ultimately limit the minimum attainable feature size. In a recent demonstration using AFM lithography, H Dai demonstrated that multiwalled carbon nanotubes could used to write lines as

narrow as 10 nm. Nanotubes have proven to be quite resistant to wear, enabling them to write large areas without tip degradation. In our work, SWNTs, 2-5 nm in diameter, were used. The smaller diameter nanotube allows sub-10-nm features to be written, while at the same time permitting larger features to be written more reliably. Lines and bits were both patterned and imaged in the tapping mode. For writing, a 5 kHz square wave of +0.5 and -9.5 V was applied to the tip. Low voltages will not induce oxidation, and very high voltages will produce excessively large features. An average tip velocity of 100 microns/sec was used to produce 8 nm lines at a 20 nm pitch. Lines as small as 6 nm in width were written at 12-15 nm spacing by adjusting the frequency of the control voltage, and the tip velocity. SWNTs allow significantly faster writing rates compared to conventional silicon cantilever tips, which typically write at rates equivalent to 5-30 bits/s when producing oxide of comparable height.

VII. Writing with Multiple Tips

Even though we have demonstrated dramatic improvements in the writing speed with a single tip, the patterning throughput (generally quoted in wafers per hour) is still too low to make SPL a viable patterning technology. We have investigated a higher-throughput lithography system where multiple probes pattern simultaneously, all scanning at speeds above 1 mm/s. In order to maintain the patterning reliability achieved in our single tip system, we require in the multiple tip system individual control of the emission current from each tip. The current feedback system used for a single tip draws the current to the preamplifier's virtual ground at the tip and applies a positive voltage to the sample. Alternatively, the current may be measured at the sample (at ground) while a negative bias is applied to the tip. In either case, the tip and sample are clearly coupled. Herein lies the challenge for multiple tip lithography.

We have successfully extended the current feedback scheme to multiple tips, where the exposing current from each tip was independently controlled. The independent current feedback allows different setpoint currents to be applied to each tip for individual dose and/or linewidth control. Multiple tip control required a new current preamplifier design with internal capacitance compensation in order to measure currents at high voltages. With these measures we were able to demonstrate parallel, current-controlled lithography of SAL601 with multiple tips.

- 1. L. P. Ghislain, V. B. Elings, C. B. Crozier, S. R. Manalis, K. Wilder, G. S. Kino, and C.F. Quate, "Near-Field Photolithography with a Solid Immersion Lens", Appl. Phys. Lett., v. 74, p. 501-503, (25 Jan 1999).
- 2. H. T. Soh, C. P. Yue, A. M. McCarthy, C. Ryu, T. H. Lee, and C. F. Quate, "Ultra-Low Resistance, Through Wafer Via (TWA) Technology and Its Applications in Three Dimensional Structures on Silicon," Jap. Jour. Appl. Phys., v. 39, p. 2393-2396, Part I, (30 April 1999).
- 3 .C. F Quate, "Nano Science and Engineering: The Next Five Years," Jour. of Nanoparticle Res., v. 1, p. 131-136. (Jan 1999).
- 4. E. M. Chow, H. T. Soh, H. C. Lee, J. D. Adams, S. C. Minne, G. Yaralioglu, A. Atalar, C. F. Quate, and T. W. Kenny "Integration of Through-Wafer Interconnects With A Two-Dimensional Cantilever Array" submitted to Sensors and Actuators, May 1999.
- 5. H. T. Soh, C.F. Quate, A. F. Morpurgo, C. Marcus, J. Kong and Hongjie Dai, "Integrated nanotube circuits: Controlled growth and ohmic contacting of single-walled carbon nanotubes", App. Phys. Ltrs., v. 75, p. 627-629, (2 Aug 1999).
- 6. K. Wilder & C. F. Quate, "Scanning probe lithography using a cantilever with integrated transistor for on-chip control of the exposing current", EIPBN99, JVST, v. B17, p. 3256-3261, (Nov/Dec99).
- 7. J. Kong, C. Zhou, A. Morpurgo, H. T. Soh, C. F. Quate, C. Marcus, H. Dai, "Synthesis, integration, and electrical properties of individual single-walled carbon nanotubes", Applied Physics A (Material Science Processing), v. A69, p. 305, (1999).
- 8. T. Sulchek, S. C. Minne, J. D. Adams, D. A. Fletcher, A. Atalar, C. F. Quate, and D. M. Adderton, "Dual integrated actuators for extended range high speed atomic force microscopy", Appl Phys Ltrs., v. 75, p. 1637-1639, (1999).
- 9. E. B. Cooper, S. R. Manalis, H. Fang, H. Dai, K. Matsumoto, S. C. Minne, T. Hunt and C. F. Quate, "Terabit-per-square-inch data storage with the atomic force microscope", Appl Phys Lett., v. 75, pp. 3566-3568, (29 Nov 1999).
- 10. T. Sulchek, R. Hsieh, J. D. Adams, G. G. Yaralioglu, S. C. Minne, and C. F. Quate, "High-speed tapping mode imaging with active Q control for atomic force microscopy", App Phys Ltrs, v. 76, p. 1473-1475, (13 March 2000).
- 11. K. B. Crozier, G. G. Yaralioglu, F. L. Degertekin, J. D. Adams, S. C. Minne, and C. F. Quate, "Thin film characterization by atomic force microscopy at ultrasonic frequencies", Appl Phys. Ltrs., v. 76, p. 1950-1953, (3 April 2000).